

Chapter 2

Continuous Monitoring of Ozone

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1.0 Introduction

It is the intent of this chapter to outline the requirements for the ambient air monitoring of ozone (O₃). All practices and procedures outlined follow the requirements set forth in 40 CFR Parts 50, 53 and 58. All agencies or groups that conduct ozone monitoring within the state of Indiana and submit data to the Air Quality System (AQS) database must follow requirements in this chapter. Indiana's ozone monitoring season is April 1 through September 30 with some sites monitoring outside this time frame.

On October 1, 2015, the United States Environmental Protection Agency (USEPA) strengthened the nation's air quality standards for ground-level ozone to improve public health and environmental protection. The updated standards will improve air quality broadly across the country, and are particularly important for at-risk groups, which include children, people of all ages with asthma and other respiratory diseases; older adults; and people who are active outdoors, especially outdoor workers, among others. EPA also updated the Air Quality Index (AQI) for ozone and the ozone monitoring season in many states to help inform the public about daily air quality. One of the standards is described as: the 3-year average of the annual 4th highest daily maximum 8-hour ozone concentrations measured at each monitor within an area over each year must not exceed .070 ppm. Additional information on these changes can be found at <http://www3.epa.gov/ozonepollution/pdfs/20151001aqifs.pdf>

Currently all Indiana Ozone Monitoring Network analyzers operated by the Indiana Department of Environmental Management, Office of Air Quality (IDEM/OAQ) are connected to the Leading Environmental Analysis and Display System (LEADS). This Data Acquisition System (DAS) allows for remote access to the analyzers and site conditions providing information on:

- Diagnostics; such as:
 - Flow
 - Pressure
 - Temperature
- Near Real Time Ambient Ozone levels
- Quality Control Activities such as:
 - Daily zero/span checks
 - One-Point (precision) precision checks
 - Multi-point calibrations
 - Electronic operator log records retention
- Site Conditions like:
 - Inside temperature
 - Meteorological conditions

2.0 Probe Siting Criteria

For specific siting requirements for O₃ monitors and inlet probes, refer to Chapter 1 of this manual and to 40 CFR Part 58, Appendixes D and E.

2.1 Horizontal and Vertical Probe Placement

The ozone monitor inlet probe should be as close as possible to the breathing zone. Complicating factors may require that the probe be elevated. The sample inlet probe height or at least 80 percent of the monitoring path must be 2 to 15 meters above ground level. The probe or at least 90 percent of the monitoring path must also be located more than one meter vertically or horizontally away from any supporting structure, walls, parapets, penthouses, etc., and away from dusty or dirty areas.

2.2 Spacing from Obstructions

The probe must be located away from obstacles and buildings such that the distance between the obstacles and the inlet probe is at least twice the height that the obstacle protrudes above the probe. The probe would be considered to be obstructed if an imaginary line extended 30 degrees up from the horizontal and rotated 360 degrees intersects any obstruction within 30 meters. Airflow must be unrestricted in an arc of at least 270 degrees around the inlet probe and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270 degrees arc. If the probe is located on the side of a building, 180 degrees of clearance is required.

2.3 Spacing from Roads

It is important to minimize the destructive interferences of nitric oxide (NO) since NO readily reacts with O₃ (see Table 1 for separation distances between roadways and monitoring stations). The proximity of other NO_x sources such as: coal fired furnaces, parking lots, or dispersion from agricultural operations must also been taken in consideration when setting up an ozone monitoring location.

Table 1
Minimum Separation Distance Between Roadways and Sampling Probes or Monitoring Paths at Neighborhood and Urban Scales for Ozone

Roadway Average Vehicles per day	Minimum Separation (meters) *
$\leq 10,000$	10
15,000	20
20,000	30
40,000	50
70,000	100
$\geq 110,000$	250

* Distances should be interpolated based on traffic flow.

2.4 Spacing from Trees

Since the scavenging effect of trees is greater for O_3 than for other priority pollutants, strong consideration must be given to the location of an O_3 inlet probe. The sample probe, inlet, or at least 90 percent of the monitoring path must be at least 10 meters from the drip line of trees which are located in the predominant seasonal wind direction. Ideally, the probe should be at least 20 meters from the drip line of trees in all directions.

3.0 Monitoring Methodology

All methods used to monitor O_3 must be a Federal Reference Method (FRM) or equivalent procedure described in 40 CFR Part 53. For all analyzers, refer to the manufacturer's instruction manual for specific requirements.

3.1 Monitoring Principles

3.1.1 Ultraviolet (UV) Absorption

This method used to monitor O_3 , is based on the Beer-Lambert principle that O_3 absorbs ultraviolet light. The greatest absorbance takes place at the 253.7 nm wavelength. A low pressure mercury vapor lamp produces light at this wavelength. This light is admitted into a measuring cell. Ozonated (sample) air and non-ozonated (zero) air are alternately passed through the sample cell. The UV radiation passes through the sample and is absorbed by ozone. The strength of the UV signal detected after passing through the sample air is directly proportional to the O_3 concentration.

3.1.2 Chemiluminescence

The State has one site which uses this method for ozone measurement. An analyzer is designed to measure the concentration of ozone using the chemiluminescence reaction of ozone with NO. The reaction of ozone combined with NO results in electronically excited NO₂ molecules. The excited NO₂ molecules release their excess energy by emitting a photon $h\nu$ and dropping to a lower energy level. It has been shown that the number of emitted photons is directly proportional to the O₃ concentration in the sample stream.

3.2 Monitoring Requirements

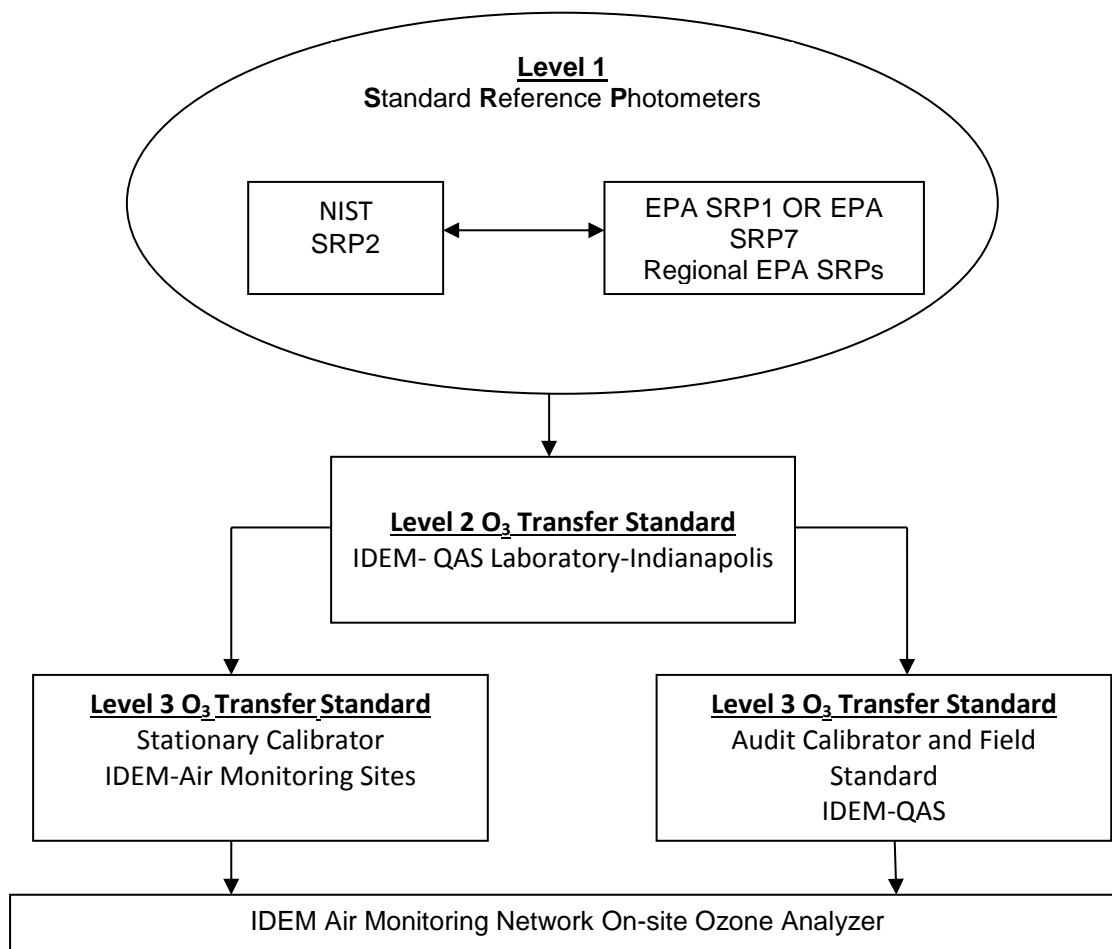
- The sample manifold and all contact sample lines and connectors must be borosilicate glass or Teflon
- The analyzer reads mercury vapor as ozone, therefore the analyzer should not be placed in a facility where mercury contamination is possible (i.e. laboratories)
- Airflow to the monitoring system should be unrestricted
- The incoming sample air should not be pressurized
- The location of the monitor should be maintained at a temperature between 59° and 91.4° Fahrenheit

4.0 Calibration Methodology

Once each year, prior to the beginning of the ozone monitoring season, the OAQ O₃ Standard is verified at the USEPA's Region V laboratory facility. There, the IDEM O₃ Standard is compared to the EPA Level 1 Standard Reference Photometer. Upon successful verification, the OAQ's standard becomes a Level 2 standard and serves as the Primary Standard used to verify/certify other ozone standards, thus making those a Level 3 transfer standard. The OAQ also has a backup standard verified against the EPA Level 1 Standard Reference Photometer.

A transfer standard is defined as a transportable device or apparatus which, together with associated operational procedures, is capable of accurately reproducing pollutant concentration standards (in this case, ozone) or of producing accurate assays of pollutant concentrations which are quantitatively related to a higher level and more authoritative standard. The transfer standard's purpose is to transfer the authority of a Level 1 pollutant standard (in this case, ozone) to a remote point where it is used to verify or calibrate an air monitoring analyzer. (see Figure 1)

Figure 1
Ozone Standard Tractability Ladder



Routine calibrations of the IDEM ozone monitoring network analyzers are performed every three months (USEPA requires 6 months) using the on-site Level 3 O₃ transfer standard. Heretofore this term can be considered synonymous with: station calibrator.

The station calibrators are calibrated then verified against the IDEM Level 2 O₃ Primary Standard once each year in the IDEM QA laboratory. The calibration consists of adjusting the zero and offset of the calibrator while comparing it to the Primary Standard. Following this two point calibration, the verification is started and consists of a six day comparison using a zero and five upscale points. Six months after the laboratory verification the station calibrators are verified in the field by a Level 3 Transfer Standard (Field Standard) or by a designated Level 2 Field Primary Standard. For more information on transfer standards see Chapter 6 of this manual or consult: <http://www.epa.gov/ttn/amtic/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf>

All calibrations must follow the guidelines established in 40 CFR Part 50 Appendix D.

4.1 Calibration Environment

In order to ensure an ozone calibration is done accurately, certain conditions must be met:

- The verification/certification of the O₃ transfer standard must be current (see Chapter 6)
- The O₃ transfer standard must have ample warm up time (15-30 minutes)
- The dilution air must be dry, free of nitrogen oxides, ambient O₃ and traces of mercury
- The station temperature must be between 59° and 91.4° Fahrenheit

4.2 Determination of Standard Concentration

Use the following formula to determine O₃ concentrations (NOTE: site calibrators that meet verification requirements do not use the established slope and intercept; only calibrators that are transported to and from the sites use an established slope and intercept to mathematically calculate the standard ozone output):

$$\text{Standard Concentration} = 1/\text{slope} \times (\text{Indicated O}_3 \text{ Value} - \text{Intercept})$$

The slope and intercept are determined during the verification/certification of the ozone transfer standard. See Chapter 6 of this manual for the verification/certification procedures.

4.3 Calibrations

Calibrations should be carried out at the field monitoring site by allowing the analyzer to sample test atmospheres containing known pollutant concentrations. The analyzer to be calibrated should be in operation for at least several hours (preferably overnight) prior to the calibration so that it is fully warmed up and its operation has stabilized. During the calibration, the analyzer should be operating in its normal sampling mode, and it should sample the test atmosphere through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and through as much of the ambient air inlet system as is practicable. All operational adjustments to the analyzer should be completed prior to the calibration.

4.3.1 On-Site Multi-Point Calibration

There may arise special case situations which would require IDEM, an external contractor, local agency or industrial network to sample for ozone without advance monitoring or data acquisition systems (DAS). In these cases it would be necessary to perform the multi-point calibration on site using the procedure outlined below.

A data validation audit should be conducted prior to any routine recalibration. This one-point audit (.350-.450 ppm O₃) must be conducted prior to any analyzer adjustments. The purpose of

the audit is to determine the validity of the data from the last audit or calibration to the present date.

Observe the following steps when performing a multi-point calibration on a UV absorption or Chemiluminescence ozone monitor:

- Attach the analyzer's sample line to the vented output of the calibrator. A vented output consists of a union tee to bleed off excess pressure or an output manifold on the calibrator. If excess flow pressure is not released, the analyzer could be damaged. Adjust the zero air flow from the calibrator to the analyzer. The zero air flow must exceed the analyzer's total flow demand by at least 25% to ensure that no ambient air is pulled into the system through the vent. For example, if the analyzer flow demand is 1.0 l/min then the total output flow from the calibrator should be no less than 1.25 l/min.
- Allow for stabilization (a response is considered stable when the display does not vary more than 5 ppb over a five minute period). Using the analyzer's zero adjustment; adjust the analyzer response to read .000 mV or ppm on the data acquisition system (DAS). Record the zero response on the calibration worksheet; an example of which can be found.
- Using the O₃ standard concentration equation below and the calibrator certification information, determine the calibrator settings required to generate a concentration at approximately 80% of the analyzer's range (e.g., for an analyzer operating in the 0-.5 ppm range, .400 to .450 ppm should be used as the span concentration).

$$\text{Std. Conc. (ppm)} = \text{Slope} \times (\text{indicated O}_3 - \text{intercept})$$

Allow the analyzer to sample until the response is stable. Adjust the span setting until the response matches the standard concentration determined in the above equation (to within $\pm 2\%$).

- After the zero and the 80% of range concentration have been set, make no further adjustments to the zero or span controls. Three additional concentrations must be introduced (e.g., .300, .200 ppm and .090 ppm). Record or enter the standard concentration (those introduced by the O₃ generator or photometer) and the analyzer's indicated response on the calibration worksheet/spreadsheet.
- Determine the calibration slope by:
 - a. Using the least squares linear regression method to find the line of best fit. Use analyzer responses (in ppm) as the X values. Use the standard ozone concentrations (generated from a certified ozone generator or photometer) in ppm as Y values.
 - b. Adjust the analyzer's span pot so that the slope is a fixed value (i.e., for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 for a 100 millivolt

or strip chart output; a 0.0005 slope for a 1000 millivolt). All calibration concentrations must be within $\pm 2\%$ of the range of the monitor.

- Calculate the measured concentration using the observed concentrations and the calibration slope and intercept.
- Compare the difference between the measured and standard concentrations. If any point is outside the 2% or range limit, the calibration is considered invalid and must be repeated. If a successful calibration cannot be completed in two attempts, the instrument is considered suspect, and maintenance may be required.

4.3.2 On-Site Multi-Point Calibration using the station calibrator

Manual field calibrations of ozone analyzers are performed at the individual monitoring sites using the Level 3 verified station calibrator. The analyzer is challenged to sample test atmospheres containing a known concentration of ozone and zero air.

To perform an ozone field calibration, it is not necessary to change the set-up of the calibrator delivery system. To begin the calibration:

- Log into the station laptop and access the data logger
- From the User menu, Press G to display channel identification numbers
- Press C and the ozone channel number/Q to disable the ozone channel and flag the data
- Press U to return to the User Menu
- Press: MENU on the analyzer, and using the arrow keys, select: INSTRUMENT CONTROLS
- Press: ENTER
- Using the arrow keys, select: SERVICE MODE
- Press: ENTER twice to turn ON the SERVICE MODE
- Press: MENU twice to return to the MAIN MENU
- Using the arrow keys, select: CALIBRATION
- Press: ENTER
- Select: CALIBRATE ZERO

- Press: ENTER
- Introduce zero air to the analyzer by setting the station calibrator to Level 60
- Allow for stabilization
- Press: ENTER to set the zero, the analyzer will automatically save the new zero value
- Press: MENU on the analyzer
- Using the arrow keys, select: CALIBRATE O₃
- Press: ENTER
- Introduce a concentration of .400 ppm ozone to the analyzer by setting the station calibrator to Level 66
- Allow for stabilization
- Using the arrow keys, set the analyzer ozone response to match the calibrator display
- Press: ENTER to save the setting
- Press: MENU twice to return to the MAIN MENU
- Using the arrow keys, select: INSTRUMENT CONTROLS
- Press: ENTER
- Using the arrow keys, select: SERVICE MODE
- Press: ENTER twice to turn OFF the SERVICE MODE
- Press: RUN on the analyzer to return to normal sampling mode
- Introduce three more evenly spaced ozone concentrations (e.g., .300 ppm, .200 ppm, and .090 ppm) using the same procedure that was used to produce a .400 ppm concentration
- All calibration points must be within $\pm 2\%$ of the full range of the analyzer (e.g., if the range is .500 ppm, then all measured values must be within $\pm .010$ ppm of the introduced test concentration)
- Set the station calibrator to Level 99 to return it to STANDBY mode

- Enable the ozone channel on the station Zeno data logger and make the appropriate electronic operator log entries

4.3.3 Remote Multi-point Calibration using LEADS to control the Station Calibrator

Currently all O₃ sites in the IDEM continuous air monitoring network are equipped with on-site Teledyne Advanced Pollution Instruments (API) mass flow calibrators. These units can be accessed remotely through the Leading Environmental Analysis and Display System (LEADS). Calibrations and certain quality assurance/quality control processes are conducted telemetrically on a routine pre-set schedule and/or on a by demand basis.

A Multi-point Calibration consists of a zero and four upscale points, the highest being above the NAAQS (for SLAMS criteria pollutants) and higher than any routine values one might expect at the site. The remote multi-point calibration should include:

- A zero concentration (pollution free air)
- A concentration between 80% and 90% of full range (or, approximately .400 ppm for a .500 ppm range ozone analyzer)
- Three more concentrations spread evenly across the operating range (or, approximately .300 ppm, .200 ppm and .090 ppm for a .500 ppm range ozone analyzer)

This multi-point calibration must be performed at the time of the initial installation and after a six month period (Note: IDEM calibrates on a three month cycle using the LEADS automatic setup) has lapsed since the most recent multi-point calibration. All calibration points must be within $\pm 2\%$ of the full range of the analyzer (e.g., if the range is .500 ppm, then all measured values must be within $\pm .010$ ppm of the introduced test concentration).

4.3.4 Multi-point Calibration Frequency

A multi-point calibration should be performed on an analyzer if any of the following conditions exist:

- Following any repairs (replacement of electronic boards, optics, etc.) that may affect the calibration
- Physical relocation of the analyzer
- After initial installation
- At the beginning of each monitoring season
- After a six (6) month period has lapsed since the most recent Multi-point Calibration

- Any time zero and span checks show significant drift indicating the current calibration may have changed

5.0 Quality Control Checks and Quality Assurance Audits

Quality control checks and quality assurance audits are performed to ensure the validity of the data submitted. Results of these audits are also used to calculate the Precision and Accuracy (P&A) of a monitor or network. The Quality Assurance Section (QAS) submits quarterly reports of the statewide P&A data to USEPA through the Air Quality System database (AQS). See Chapter 13 of this manual for specific instructions on how to calculate and report P&A values.

5.1 Zero/Span/One-Point Quality Control Check

Daily zero and span checks are ran. These checks are used to catch analyzer drift and to help determine data validation. These quality control measures are intended to further ensure high quality monitoring data and to prevent unnecessary data loss. Once a week, a one-point quality control check (precision audit) is done along with the daily zero and span check. Currently, all continuous ozone analyzers are routinely audited remotely through the LEADS during season of operation. Indiana's ozone season runs from March 1 through October 31, with some sites operating longer. The zero, span and precision one-point quality control check are scheduled by the OAQ/AMS/LEADS Administrator and are set to run at midnight when ambient ozone levels could be expected to be at a low. The span concentration is .400 ppm O₃ and the precision level check is .090 ppm O₃. For data validation, the span and the precision one-point quality control check must be $\leq \pm 7\%$; if not, determine if maintenance is needed and then run a multi-point calibration.

On-site manual precision audits may be conducted by IDEM quality assurance staff on an as needed basis such as:

- LEADS communication malfunction
- Unstable or failing remote audit results

5.2 Quarterly Accuracy Audit

Once each quarter during the monitoring season IDEM quality assurance staff conduct accuracy audits on each ozone analyzer in the network. This audit frequency is more than the USEPA requires (40 CFR Part 58, Appendix A). For valid data, the percent difference of audit levels 3-10 must be $\leq \pm 15\%$ and audit levels 1&2 ± 1.5 ppb or $\pm 15\%$. An accuracy audit consists of 3 test concentrations in the ranges listed below and a zero:

For analyzers set to sample in the 0-.5 ppm range:

- .190 - .259ppm O₃
- .140 - .169ppm O₃

- .070 - .089ppm O₃

5.2.1 Procedure

The procedure outlined below is to be used for Indiana Ozone Monitors equipped with the LEADS. If the LEADS is not in service or another form of DAS is being utilized, flag the data with the appropriate information according to the procedure recommended by the specific DAS operations manual.

Once on site, to begin the audit:

- Plug in the audit calibrator and allow for warm up (30 minutes)
- Log into the station laptop and access the data logger
- From the User menu, Press G to display channel identification numbers
- Press C and the ozone channel number/Q to disable the ozone channel and flag the data
- Press U to return to the User Menu
- Press T
- Press R/ozone channel number to view the current voltage output
- Open the OAMD O₃ Audit form on the field laptop
- Fill in the appropriate information including:
 - a) Site Name
 - b) Auditor
 - c) Date
 - d) Start time
 - e) Analyzer calibration slope and intercept
 - f) Audit and On-Site Calibrator serial numbers
- Introduce zero air to the analyzer by setting the audit calibrator to zero
- Disconnect the incoming sample line at the manifold and cap the port
- Attach the incoming sample line to the output of the calibrator, venting if necessary
- Allow for stabilization

- Observe the Zeno output display in volts
- Enter the output and the calibrator zero response on the OAMD form. The Oracle spread sheet will automatically calculate the Zeno output to parts per million ozone and display the % difference between the standard and observed concentration
- Introduce a test concentration of between .190 and .259 ppm O₃ to the analyzer
- Allow for stabilization
- Observe the Zeno output display in volts
- Enter the output and the calibrator response on the OAMD field data form. The Oracle spread sheet will automatically calculate the Zeno output to parts per million ozone
- Introduce a test concentration of between .140 and .169 ppm O₃ to the analyzer
- Allow for stabilization
- Observe the Zeno output display in volts
- Enter the output and the calibrator response on the OAMD field data form. The Oracle spread sheet will automatically calculate the Zeno output to parts per million ozone
- Introduce a test concentration of between .070 and .089 ppm O₃ to the analyzer
- Allow for stabilization
- Observe the Zeno output display in volts
- Enter the output and the calibrator response on the OAMD field data form. The Oracle spread sheet will automatically calculate the Zeno output to parts per million ozone and display the % difference between the standard and observed concentration
- Reconnect the incoming sample line to the manifold and disassemble the audit calibrator
- Allow the ozone analyzer to return to ambient conditions
- Enable the ozone channel and make the appropriate electronic operator log book entries
- Enter the audit end time on the OAMD form and save the audit results

6.0 Quality Control Measures

6.1 Zero Span Checks

Daily zero/span (.400 ppm O₃) checks of all IDEM monitoring network ozone analyzers are conducted remotely using the LEADS (see Section 5.0). This allows AMS and QAS staff members to closely track the stability of the ozone analyzers.

If an instrument does not have the LEADS or some other internal or automatic capacity, this zero/span must be done manually at least once every two weeks. If the analyzer drifts excessively, more frequent zeros and spans will be required. Zero drift should be $\leq \pm 3.0$ ppb for a 24 hour period and $\leq \pm 5.0$ ppb for a time period greater than 24 hours up to 14 days. The span drift should be no more than $\pm 7\%$. Although not used specifically for data validation/invalidation, zero/span checks will help to track a monitor's drift pattern and may show at what particular point a monitor began to show a trend. If an audit exceeds the allowed percent difference and records of zero/span checks can be supplied to identify when excessive drift began, it may not be necessary to invalidate an entire operational period. Decisions on data validation are made by the QA Section Chief. See Chapter 11 of this manual for zero/span drift limits.

6.2 Site Checks

Once every two to three weeks physical site checks are performed by AMS staff to verify the actual operating/environmental conditions of the ozone monitoring site. Although with LEADS diagnostics can be checked remotely, it is still necessary to change the inline particulate filters and clean air scrubbers on a routine basis. Also, the site check allows for:

- Physical inspection of incoming sample lines (sample lines should be replaced on a 1 to 4 year cycle, depending on how dirty the site becomes and if thru the probe audits indicate an issue)
- Weed abatement
- Heating and air conditioning system inspection
- Safety inspection
- General housekeeping
- The condition of the sample probe line and manifold. The sample probe and manifold should be scheduled for cleaning bi-annually or be cleaned any time visible deposits of dirt can be detected. Avoid using cleaning solutions containing soap, alcohol or other products containing hydrocarbons
- Changes to the area such as ongoing construction

- Vandalism

6.3 Preventive Maintenance

Preventive maintenance is an intrinsic part of quality control. Analyzers and station calibrators must have routine preventive maintenance performed to ensure proper operation and prevent data loss or costly repairs.

Most manufacturers supply a preventive maintenance check list with the analyzer's instruction manual. A tracking mechanism such as a computerized database or an on-site check list should be developed to ensure all maintenance is performed as recommended. This tracking mechanism needs to be reviewed and updated as new equipment or operating procedures are put in place.

All maintenance should be logged into the electronic or bound logbooks located at each monitoring site.

7.0 Data Reduction and Reporting

The NAAQS for ozone is based on hourly average concentration. These hourly average concentrations are done automatically via the LEADS. If this reduction must be done manually, refer to Chapter 12 of this manual for specific guidelines.

Form 1 OAMD O₃ AUDIT

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Calib. Settings	Calib. (in ppb)	Monitor response			Measured conc. (in ppm)	Standard conc. (in ppm)	% Diff.	
		DVM Units:	Primary Units:	Secondary Units:			Primary	Secondary

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Calibration pot information:

Zero Pot: Span Pot:

For TECO Only:									
A/B Test:									
Are the 10 averages within 3.0%? : (Circle one) Yes No									

Leak Test: Site Temp: Reminder: IS PSI SET IN COMPUTER?

DIAGNOSTICS

TECO					DASIBI	
Flow:	A:		B:		Flow:	
For 49:						
Noise:	A:		B:		Sample Frequency:	
Frequency	A:		B:			
Pressure:	A:		B:		Control Frequency:	
Temp:	A:		B:			
For 49C:					(Also for 1008):	
Intensity:	A:		B:		Temperature:	
Noise:	A _{ref}		A _{sam}		B _{ref}	B _{sam}
Pressure:						
Bench:						
Bench lamp:						

COMMENTS
